Some Laser-induced Reactions in the Gas Phase

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WE report some preliminary studies in which a ruby laser initiates chemical reactions in the gas phase, by three mechanisms:† (*a*) direct heating of a solid by focussed laser beam, causing vaporization; (*b*) focussed-laser gas-spark (dielectric breakdown); and (*c*), photodissociation.

The reaction of carbon and hydrogen [type (*a*)], yielded acetylene (>90%) together with methane, ethylene, methylacetylene, allene, and buta-1,3-diyne. For several different irradiations (100—4000 laser shots), acetylene was always the first product detectable and always the major component. This is apparently the first laser synthesis of hydrocarbons from carbon and hydrogen. Epstein and Sun[1] performed a similar experiment, but because the number of laser shots was small, no products were detected.

The reactions carbon–chlorine, silicon–hydrogen, and germanium–hydrogen were also of type (*a*). The products of these reactions were CCl_4, SiH_4, and GeH_4, respectively (i.r.). Higher molecular weight compounds were not formed in detectable amounts.

Of the type (*b*) reactions N_2–O_2 and N_2–H_2, the first gave N_2O and NO_2 in equilibrium with N_2O_4. The other nitrogen oxides are less stable and probably occur as intermediates. Both free nitrogen and free oxygen atoms may be involved as both are produced in the laser spark, where electric-field strengths[2] are of the order of 10^8 v/cm. In contrast, there were no detectable products for N_2–H_2, for irradiations up to 4000 shots. This is reasonable as it has been shown[3] that there is no reaction of ground-state N with H_2. Similarly, only ^2P H will react with N_2.[4] Apparently excited states are not formed under our conditions or decay very quickly.

Two type (*c*) systems, Cl_2–H_2 and Cl_2–CH_4, were studied, and gave HCl, and HCl and all possible chloromethanes, respectively. Light was excluded, and the laser beam was filtered to remove the pump light. We believe that these reactions involve the known chain reactions initiated by the photodissociation of chlorine into chlorine atoms. However, the most reasonable mechanism for photodissociation is a simultaneous two-photon absorption, which, at 3473 Å, would occur within the one-photon band 2400—4200 Å. Although these two spectra cannot be the same (since the selection rules are different for centrosymmetric molecules), considerable overlap could occur.

These experiments demonstrate the versatility of laser-induced reactions. The main application will be in determining rates and mechanisms for fast reactions and the detection of short-lived intermediate species.

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† A rotating prism Q-switched ruby laser operating at one pulse/sec. was used for all experiments. Peak power was adjustable from 1 to 12 Mw. Analysis of products was obtained on a Beckman IR-12, in the irradiation cell.

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